JOURNAL OF MATERIALS SCIENCE 10 (1975) 658–660

The growth of germanium precipitates in an Al–4.0 wt % Ge alloy

H. KÄHKÖNEN, P. SUHONEN
Department of Physics 2, University of Turku, Finland

The growth of germanium precipitates in an Al–4.0 wt % Ge alloy aged at 145, 160 and 190° C has been studied by small-angle X-ray diffraction. The intensity curves show that the precipitates are not spherical. By assuming that the precipitates are long cylindrical rods the experimental and theoretical intensity distributions are in a good agreement. The radius of the rods was determined as a function of ageing time.

1. Introduction

Precipitation phenomena in Al–Ge alloys have been recently studied by X-ray, electron-microscopic, resistivity and hardness methods [1-6]. According to X-ray measurements the precipitates consist of pure germanium [4]. Because the size of the precipitates is very small, small-angle X-ray scattering is a suitable method by which to study the precipitation phenomenon. Beller and Gerold [1] and Beller [2] have measured small-angle X-ray scattering from Al–Ge specimens at scattering angles $2\theta > 1°$. From these measurements they have determined the average spherical radius of the Ge-clusters. Kuznetsova *et al.* [4] have found that the small-angle X-ray scattering mainly appears at angles $2\theta < 1°$. They also observed a maximum of scattering intensity at about $2\theta = 0.5°$ for a quenched specimen. The maximum disappears, when the specimen is annealed.

Sorokin and Sitnikova [5] have studied the diffuse scattering of X-rays by single crystals of an Al–Ge alloy at the stage of decomposition corresponding to the attainment of maximum hardness. Their preliminary electron-microscopic examination shows that at this stage the Ge precipitates are platelets 70 to 100 Å thick and ~ 450 Å long. Koester [6] has observed in his electron-microscopic study that rod-shaped particles are formed by 250° C ageing.

In the present work small-angle X-ray scattering by Al–4.0 wt % Ge specimens has been studied at scattering angles $2\theta \geqq 0.08°$, when the specimens were aged at 145, 160 and 190° C.

2. Theoretical considerations

The experimental intensity curves show that the small-angle X-ray scattering of Al–Ge specimens cannot be interpreted by considering spherical precipitates. If we assume that precipitates are narrow cylinders of diameter $2R$ and length $2H$, the scattering intensity can be expressed as [7]

$$E'(l) = \frac{K}{Hl}\exp(-\pi^2R^2l^2/\lambda^2r^2), \qquad (1)$$

where the scattering angle $2\theta = l/r$, λ = the wavelength of the radiation and K is a constant. If we use a slit system, then

$$\begin{aligned} E(l) &= \frac{2K}{H}\int_0^\infty \frac{\exp[-\pi^2R^2(l^2+y^2)/\lambda^2r^2]}{\sqrt{(l^2+y^2)}}\,\mathrm{d}y \\ &= \frac{K_1}{H}\exp(-\pi^2R^2l^2/2\lambda^2r^2) \\ &\qquad K_0(\pi^2R^2l^2/2\lambda^2r^2), \qquad (2) \end{aligned}$$

where K_0 is a modified Besselian function [8]. The asymptotic expansion of K_0 for large arguments is

$$\begin{aligned} K_0(z) &\approx \sqrt{\left(\frac{\pi}{2z}\right)}\,\mathrm{e}^{-z}\left[1 - \frac{1}{8z}\right. \\ &\quad \left. + \frac{9}{2!(8z)^2} - \ldots\right] \approx \sqrt{\left(\frac{\pi}{2z}\right)}\mathrm{e}^{-z}. \qquad (3) \end{aligned}$$

Thus, the scattering intensity can be expressed by the approximative formula

$$E(l) \approx \frac{K_2}{Hl}\exp(-\pi^2R^2l^2/\lambda^2r^2). \qquad (4)$$

The value of R can be calculated by the Guinier approximation

$$R = \frac{\lambda r}{\pi}\sqrt{\left(\frac{\ln\{[E(l)l]_1/[E(l)l]_2\}}{l_2^2 - l_1^2}\right)}. \quad (5)$$

The study of the function $K_0(z)$ reveals that Equation 4 can be used, when the radius R is not too small.

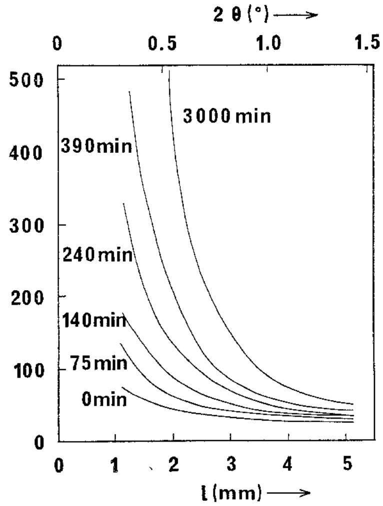

Figure 1 Small-angle X-ray scattering intensity $E(l)$ versus l for a specimen aged at 145°C.

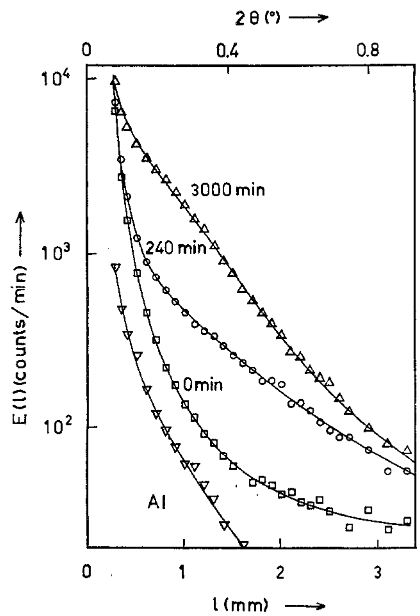

Figure 2 Small-angle X-ray scattering intensity $E(l)$ versus l for an aluminium specimen and an aluminium-germanium specimen aged at 145°C.

3. Experimental results and discussion

The Al–4.0 wt % Ge specimens were prepared from super-purity aluminium and germanium (99.999%, Koch Light Laboratories Limited, England). The specimens were homogenized for several hours at 470°C, and then quenched in water at room temperature. The ageing temperatures were 145, 160 and 190°C. Diffraction measurements were performed, using a Kratky X-ray small-angle scattering camera in combination with a programmed step scanning device. Cu$K\alpha$ radiation was used for the measurements. All the intensity curves were corrected for the background scattering.

We initially attempted to discover a maximum scattering intensity at 0.5° [4]. No maxima were found as Fig. 1 shows. Perhaps this is due to the homogenizing temperature, which was 70°C higher than that of Kuznetsova *et al.*

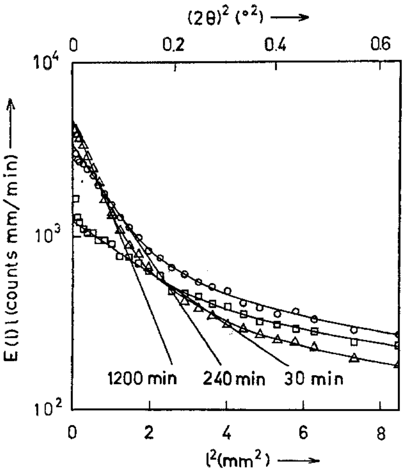

Figure 3 Three examples of the determination of the mean radius of the cylinders for specimens aged at 190°C.

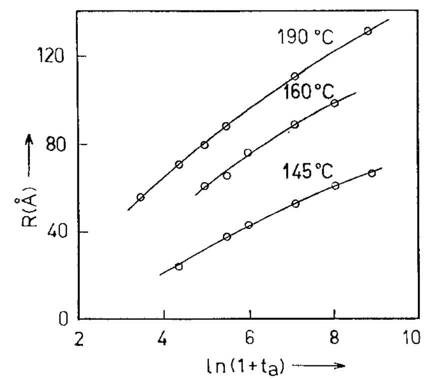

Figure 4 The change in zone radius R during isothermal ageing at 145, 160 and 190°C. t_a = ageing time in min.

To be able to measure the scattering intensity at very small angles the entrance slit of the camera was reduced from 81 to 60 μm. Measurements could be performed down to $2\theta = 0.08°$: an example of these measurements is shown in Fig. 2. The scattering intensity increases rapidly with decreasing scattering angle. This scattering effect is due to germanium clusters, as the scattering intensity from a corresponding pure aluminium specimen is very small (Fig. 2).

In calculating the volume fraction of the precipitates from intensity curves we need the extrapolated value of the scattering intensity at $2\theta = 0°$ [1, 2, 4]. Because of the very steep rise of the intensity curves at very small angles, the extrapolation is quite ambiguous. We also attempted to determine the integrated scattering intensities, but for the reason mentioned above we could not accurately estimate the values of $E(l)l$ at angles below 0.08°.

By plotting $\ln E(l)$ versus l^2 we found that the curves do not obey the Guinier approximation. Next we applied the theory described above and an example of the curves $\ln[E(l)l]$ versus l^2 is shown in Fig. 3. The mean radius of the zones was calculated from Equation 5. The radius increases with ageing time at 145, 160 and 190° C as Fig. 4 indicates. For a quenched specimen the curve $\ln[E(l)l]$ versus l^2 had no linear portion and the zone radius could not be determined.

Our small-angle X-ray scattering measurements show that the germanium precipitates in Al–4.0 wt % Ge alloy are not spherical and we assumed that the precipitates are long cylindrical rods. Figs. 1 to 3 show that the experimental results agree with this model. This result supports the electron-microscopic study of Koester [6] and the assumption made by Sorokin and Sitnikova [5] that the Ge precipitates could be long platelets.

Acknowledgements

The authors wish to thank Mr P. Sjöholm, for his help in the measurements. The grant received from the Finnish State Committee for Natural Science in support of this study is gratefully acknowledged.

References

1. M. BELLER and V. GEROLD, *Z. Metallk.* **61** (1970) 659.
2. M. BELLER, *ibid* **63** (1972) 663.
3. M. BELLER, P. FÜRNROHR and V. GEROLD, *Phys. Stat. Sol.* (*a*) **17** (1973) 435.
4. R. I. KUZNETSOVA, V. I. RANYUK and S. Z. FEDORENKO, *Fiz. Metal. Metalov.* **35** (1973) 937.
5. L. M. SOROKIN and A. A. SITNIKOVA, *Sov. Phys. Solid State* **9** (1968) 1525.
6. U. KOESTER, *Mat. Sci. Eng.* **5** (1970) 174.
7. A. GUINIER and G. FOURNET, "Small-Angle Scattering of X-Rays", (Wiley, New York, 1955) p. 27.
8. H. KÄHKÖNEN and O. KARVINEN, *Ann. Acad. Sci. Fenn.* **A VI** (1970) 340.

Received 29 August and accepted 9 September 1974.